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(21) International Application Number: PCT/US91/04771 (22) International Filing Date: 10 July 1991 (10.07.91) (30) Priority data: 551,123 11 July 1990 (11.07.90) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: STEPHENSON, Charles, H. ; Route 2, Box 636, McKenney, VA 23872 (US). YANG, Hung, Han ; 322 Harwick Drive, Richmond, VA 23236 (US). (74) Agents: SULLIVAN, Daniel, W. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: A METHOD FOR IMPROVING THE HYDROLYTIC RESISTANCE OF ARAMID FIBER (57) Abstract A process for improving the hydrolytic resistance of aramid fiber, particularly poly(p-phenylene terephthalamide) fiber is disclosed. The process comprises coating aramid fiber with an aqueous fluoropolymer dispersion and drying the fiber while curing the coating to its surface.		

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TITLE

A METHOD FOR IMPROVING THE
HYDROLYTIC RESISTANCE OF ARAMID FIBER

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention provides a process for improving the hydrolytic resistance of aramid fiber by coating such fiber with an aqueous fluoropolymer dispersion. The invention also contemplates poly(p-phenyleneterephthalamide) aramid fiber having improved hydrolytic resistance.

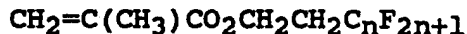
Description of the Prior Art

It is known in the art that coating aramid fiber with fluorocarbon containing material improves certain physical and chemical properties of the fiber.

For example, Trask, United States Patent, 4,232,087 discloses a method of coating "Nomex" aramid fibers with a dispersion comprised of polytetrafluoroethylene particles in the presence of water and a water soluble chromium complex of a long chain fluorochemical to improve the air permeability, acid resistance, water repellency, and oil repellency of the fibers.

Sasaki et al., United States Patent, 4,337,155 discloses preparing an emulsion of a fluorine-containing polymeric resin and then coating the emulsion onto wholly aromatic polyamide fiber material to improve the air permeability and acid resistance of the material.

Fasick et al., United States Patent, 3,378,609, the disclosure of which is specifically incorporated herein by reference, discloses compositions based upon homopolymers or copolymers derived from the monomer,



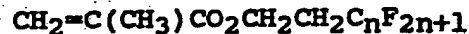
wherein n is 3 to 14. The compositions may then be applied as a water dispersion to provide oil and water

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repellent properties to films, fibers, yarns, fabrics, and other articles.

SUMMARY OF THE INVENTION

Despite the development of different fluorocarbon containing coatings for different fibers, there is still a need to provide a suitable coating to improve the hydrolytic resistance of aramid fiber. The present invention relates to treating aramid fiber with a dispersion of fluoropolymer in water, in order to improve the hydrolytic resistance of such fiber. The invention provides a process of uniformly coating aramid fiber with an aqueous dispersion comprising a polymer of ethylenically unsaturated monomers, a major proportion by weight of which is at least one fluorinated alkyl methacrylate polymer of the monomer,



wherein n is 3 to 14. Preferably, the polymer is a copolymer derived from about 75% by weight of the aforementioned fluorinated methacrylate monomer and about 25% by weight of a non-fluorine containing monomer such as 2-ethylhexylmethacrylate. The fiber is then dried while the coating is cured to its surface, preferably by heating the fiber for 15 to 60 minutes at a temperature in the range of 130°C to 170°C.

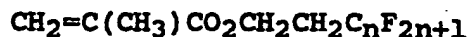
Preferably, poly(p-phenylene terephthalamide) aramid fiber is uniformly coated with a dispersion of fluoropolymer in water such that the amount of fluorocarbon containing coating is in the range of 0.25 to 2% based on total weight of the coated fiber. In a preferred embodiment, the poly(p-phenylene terephthalamide) aramid fiber thus prepared exhibits an improvement in hydrolytic resistance by greater than 20% compared to an uncoated poly(p-phenylene terephthalamide) aramid fiber.

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DETAILED DESCRIPTION OF THE INVENTION

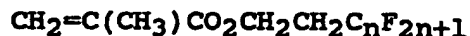
The present invention provides a process for improving the hydrolytic resistance of aramid fiber, particularly poly(p-phenylene terephthalamide) aramid fiber. The process includes uniformly coating the aramid fiber with a dispersion of fluoropolymer in water, and then drying the fiber while curing the coating to its surface.

The fluoropolymer dispersions employed in the practice of the invention are disclosed in the aforementioned Fasick et al. U.S. Patent 3,378,609. They are based on the fluorinated methacrylate monomer,



wherein n is 3 to 14. There may be used homopolymers of the aforementioned fluorinated methacrylate monomer with one or more other non-fluorine containing monomers. Copolymers of at least about 50% by weight of the fluorinated methacrylate monomer with up to about 50% by weight of one or more copolymerizable non-fluorine containing monomers may also be used. Various examples of such copolymerizable monomers and remaining monomers of the homopolymers are those disclosed in column 4, lines 3 to 57 of Fasick et al.

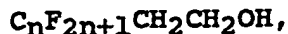
A preferred fluoropolymer of the invention is a copolymer of about 75% by weight of the fluorinated methacrylate monomer,



wherein n varies from 6 to 14 and about 25% by weight of 2-ethylhexylmethacrylate. The fluorinated methacrylate monomer is made by reacting methacrylic acid with a

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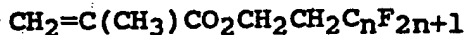
mixture of alcohols,



wherein n is 6 to 14, with an average value of about 8.

If desired, the fluoropolymer dispersion may optionally contain other polymers, such as for example a copolymer containing a small amount of a crosslinking agent.

The fluoropolymer dispersion is then applied to the aramid fiber when the fiber is either wet or dry. Any conventional coating method for example, immersing or spraying, can be used, but it is important that the dispersion is of a suitable viscosity to be uniformly applied to the fiber. The dispersion can be diluted with water, if needed. A person having ordinary skill in the art will be able to identify which dispersions have suitable viscosities. In a preferred embodiment, wet, never-dried poly(p-phenylene terephthalamide) aramid fiber which is produced according to spinning processes described in Blades, United States Patent, 3,767,756 and Yang, United States Patent, 4,340,559 is immersed in a coating bath containing the fluoropolymer dispersion at room temperature. Preferably, the coating bath is diluted to contain 1% by weight of the preferred fluoropolymer dispersion, a copolymer of about 75% by weight of the fluorinated methacrylate monomer,



wherein n varies from 6 to 14, and about 25% by weight of 2-ethylhexylmethacrylate.

After the aramid fiber is uniformly coated with the dispersion, the fiber is dried while the fluorocarbon containing coating is cured to its surface by techniques known in the art. Preferably, curing is performed by heating the fiber for 15 to 60 minutes at a temperature in

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the range of 1303 to 1703C. Longer heating periods are required with lower temperatures, and vice-versa. At 1503C, for example, a drying time of 30-60 minutes is needed. Preferably, the aramid fiber is uniformly coated with the fluoropolymer dispersion such that the amount of fluorocarbon containing coating is in the range of 0.25 to 2% based on the total weight of the coated fiber. In a preferred embodiment, the cured fluorocarbon containing coating improves the hydrolytic resistance of the aramid fiber by greater than 20% compared to an uncoated fiber.

Testing Procedures

Tensile Properties

Tenacity is reported as breaking strength divided by linear density. Modulus is reported as the slope of the initial stress/strain curve converted to the same units as tenacity. Elongation is the percent increase in length at break. Both tenacity and modulus are first computed in g/denier units which, when multiplied by 0.8838, yield dN/tex units. Each reported measurement is the average of 5 breaks.

Tensile properties for yarns are measured at 243C and 55% relative humidity after conditioning under test conditions for a minimum of 14 hours. Before testing, each yarn is twisted to a 1.1 twist multiplier (for example, nominal 1500 denier yarn is twisted about 0.8 turns/cm). Each twisted specimen has a test length of 25.4 cm and is elongated 50% per minute (based on the original unstretched length) using a typical recording stress/strain device.

The twist multiplier (TM) of yarn is defined as:

$$TM = \frac{tpi \sqrt{\text{Denier}}}{73} = \frac{tpc \sqrt{dtex}}{30.3}$$

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Wherein tpi= turns per inch and
tpc= turns per centimeter.

In the following examples, parts and percentages are by weight unless otherwise indicated.

COMPARATIVE EXAMPLE

A finish-free wet, never-dried poly(p-phenylene terephthalamide) aramid yarn was produced according to spinning processes described in Blades, United States Patent, 3,767,756 and Yang, United States Patent, 4,340,559. The aramid fiber was then tested for its hydrolytic resistance. As shown in Table I, the test yarn had a linear density of 1462 denier at 1.5 dpf (denier per filament). It gave tensile properties of 21.4 gpd (grams per denier) tenacity, 3.5% elongation at break, and 542 gpd initial modulus. A 5 m long skein of the yarn was tested for hydrolytic resistance by immersing the yarn in a 10% NaOH solution at 95°C for 20 hours. The test yarn skein was then thoroughly washed with water at room temperature and left to dry in air at zero tension. The hydrolyzed yarn gave a retained tenacity of 4.2 gpd, which was a 19.6% retention of its original tenacity. When the alkaline hydrolysis was extended to 100 hours, the hydrolyzed yarn was too weak to be tested for its tensile properties.

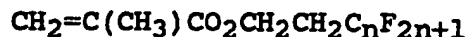
EXAMPLE I

This example illustrates the improved hydrolytic resistance of poly(p-phenylene terephthalamide) aramid yarn after such yarn is coated with a dispersion of fluoro-polymer in water.

The fluoropolymer dispersion is formed as an aqueous dispersion in water of two components, A and B. Component A is a polymer formed by the polymerization of 25% 2-ethylhexylmethacrylate with 75% of the fluorinated

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methacrylate monomer,



wherein n varies from 6 to 14 with an average of 8, together with about 0.25% each of N-methylolacrylamide and 2-hydroxyethylmethacrylate. Component B is a terpolymer of 100 parts 2-ethylhexylmethacrylate with 2 parts N-methylolacrylamide and 0.5 parts ethylene dimethacrylate. About 8 parts of A is used with about 6 parts of B to produce an emulsion having 14% solids. The fluoropolymer dispersion was added to a coating bath which was then diluted with water until the bath contained 1% of said fluoropolymer dispersion.

A 5 m long skein of the finish-free yarn used as a COMPARATIVE EXAMPLE was then immersed in the bath containing 1% fluoropolymer dispersion at room temperature for 40 hours. The yarn was uniformly coated with the fluoropolymer dispersion such that the amount of fluorocarbon containing coating was about 0.75% of the cured fiber. The yarn was then dried while the coating was cured to its surface at 150°C at zero tension for half an hour. As Table I shows, the coated yarn was subjected to hydrolysis in a 10% NaOH solution at 95°C for 20 hours. The hydrolyzed yarn gave a retained tenacity of 15.2 gpd which was a 71.0% retention of its original tenacity. When the hydrolysis was extended to 100 hours, the hydrolyzed yarn gave a retained tenacity of 7.9 gpd which was a 36.9% retention of its original tenacity.

EXAMPLE II

This example illustrates similar improvements in the hydrolytic resistance of poly(p-phenylene terephthalamide) aramid yarn when the yarn is coated with a dispersion of fluoropolymer in water. As shown in Table I, the process of EXAMPLE I was carried out except that

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the time of immersing the yarn in the coating bath containing 1% of the fluoropolymer dispersion was decreased to 1 minute. The yarn was uniformly coated with the fluoropolymer dispersion such that the amount of fluorocarbon containing coating was about 0.6% of the coated fiber. The coated yarn was subjected to hydrolysis in a 10% NaOH solution at 953C for 20 hours. The hydrolyzed yarn gave a retained tenacity of 14.7 gpd which was a 68.7% retention of its original tenacity. When the hydrolysis was extended to 100 hours, the hydrolyzed yarn gave a retained tenacity of 6.8 gpd which was a 31.8% retention of its original tenacity.

TABLE I

<u>EXAMPLE</u>	<u>COMPARATIVE</u>	<u>I</u>	<u>II</u>
Base Yarn	poly(p-phenylene terephthalamide)		
Coating Agent	None	1% "Zepel" B	1% "Zepel" B
Immersion Time	---	40 hours	1 min.
<u>AS SPUN YARN</u>			
Yarn denier	1462	1462	1462
Dpf	1.5	1.5	1.5
Tenacity	21.4	21.4	21.4
Elongation, %	3.5	3.5	3.5
Modulus, gpd	542	542	542
<u>HYDROLYZED YARN</u>			
10% NaOH/953C/20 hours			
Retained tenacity,			
gpd	4.2	15.2	14.7
% Tenacity retention	19.6	71.0	68.7
<u>HYDROLYZED YARN</u>			
10% NaOH/953C/100 hours			
Retained tenacity,			
gpd	-o	7.9	6.8
% Tenacity retention	-o	36.9	31.8

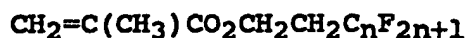
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CLAIMS:

1. A process for improving the hydrolytic resistance of aramid fiber by the steps of:

a) coating aramid fiber with an aqueous fluoro-polymer dispersion to obtain a uniform fluorocarbon containing coating on the fiber, said aqueous fluoro-polymer dispersion comprising a polymer of ethylenically unsaturated monomers, a major proportion by weight of which is at least one fluorinated methacrylate monomer of the structure,



wherein n has a value of from 3 to 14;

b) drying the fiber while curing said coating to its surface.

2. A process in accordance with claim 1 wherein said polymer is a copolymer of the fluorinated methacrylate monomer with 2-ethylhexylmethacrylate.

3. A process in accordance with claim 1 wherein the curing of the fluorocarbon containing coating to the surface of the fiber is effected by heating the fiber for 15 to 60 minutes at a temperature in the range of 130°C to 170°C.

4. A process in accordance with claim 1 wherein the aramid fiber is poly(p-phenylene terephthalamide).


5. A poly(p-phenylene terephthalamide) aramid fiber having improved hydrolytic resistance produced in accordance with claim 4 wherein the amount of fluorocarbon containing coating is in the range of 0.25 to 2% based on total weight percent of the coated fiber.

6. A poly(p-phenylene terephthalamide) aramid fiber having improved hydrolytic resistance in accordance with claim 5 wherein said fiber exhibits hydrolytic resistance by greater than 20%.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/04771

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 D06M15/277		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D06M	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0 032 744 (TEIJIN LIMITED) 29 July 1981 see the whole document & US,A,4 337 155 (SASAKI ET AL.) 29 June 1982 cited in the application ---	1-6
Y	GB,A,1 010 539 (DU PONT DE NEMOURS) 17 November 1965 see the whole document & US,A,3 378 609 (FASICK ET AL.) 16 April 1968 cited in the application ---	1-6
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 332 (C-455) 29 October 1987 & JP,A,62 115 040 (ASAHI CHEM IND CO LTD.,) 26 May 1987 see abstract --- -/-	1-6
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
2 19 NOVEMBER 1991	28. 11. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	BLAS V. 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category ^o	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 113, no. 16, 15 October 1990, Columbus, Ohio, US; abstract no. 134087U, YONETANI MASAYUKI: 'MANUFACTURE OF PARA-ORIENTED ARAMID FIBERS WITH LOW MOISTURE ADSORPTION.' page 94 ; & JP-A-02 084 508 (ASAHI CHEMICAL INDUSTRY CO., LTD) see abstract</p>	1-6

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9104771
SA 50284**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0032744	29-07-81	JP-A- 56107073	25-08-81
		US-A- 4337155	29-06-82
US-A-4337155	29-06-82	JP-A- 56107073	25-08-81
		EP-A, B 0032744	29-07-81
GB-A-1010539		BE-A- 634770	
		BE-A- 635437	
		BE-A- 645697	16-07-64
		CH-B- 404638	
		CH-B- 413580	
		CH-B- 439747	
		CH-B- 527462	30-09-69
		CH-A- 527662	
		DE-B- 1236787	
		DE-B- 1280208	
		DE-A- 1444117	06-03-69
		FR-E- 84578	
		FR-A- 1327328	
		FR-A- 1333768	
		FR-A- 1356923	
		GB-A- 971732	
		GB-A- 1011612	
		US-A- 3256230	
		US-A- 3282905	
		US-A- 3378609	
US-A-3378609		BE-A- 634770	
		BE-A- 635437	
		BE-A- 645697	16-07-64
		CH-B- 404638	
		CH-B- 413580	
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		CH-B- 527462	30-09-69
		CH-A- 527662	
		DE-B- 1236787	
		DE-B- 1280208	
		DE-A- 1444117	06-03-69
		FR-E- 84578	
		FR-A- 1327328	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9104771
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3378609		FR-A- 1333768 FR-A- 1356923 GB-A- 971732 GB-A- 1010539 GB-A- 1011612 US-A- 3256230 US-A- 3282905	